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# SEARCH FOR HIGHER TEMPERATURE SUPERCONDUCTORS

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Using a special furnace capable of applying high oxygen partial pressures, samples of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$  were prepared. In this synthesis, oxygen partial pressures up to 15 Kbar thermodynamically favored the formation of higher valences of copper and correspondingly lower concentrations of oxygen vacancies. Large regions of phase separation were discovered at large  $x$ . Preparation conditions were modified in order to synthesize only single phase materials. Valences of copper up to  $\text{Cu}^{+2.65}$  were achieved, compared with previous values of  $\text{Cu}^{+2.35}$ . Correspondingly, samples without oxygen vacancies were obtained up to  $x=0.65$ , almost doubling the range of potential superconducting copper oxides in this material system. Over the range of new compounds,  $0.35 \leq x \leq 0.65$ , no superconductivity was observed above 7K.

## INTRODUCTION

One of the simplest High  $T_C$  materials systems is  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ . This system is well known<sup>1</sup> to form a solid solution over the entire range of composition  $0 \leq x \leq 1.3$ , and yet measurements of the superconducting properties are only available over the much narrower range of  $0 \leq x \leq 0.35$  (Figure 1). This leaves a vast range of compositions with unknown superconducting behavior.

Of course, the reason that these materials remain unexplored is because there are important material complications that make it very difficult to synthesize these samples. As the Sr content is increased, the copper valence increases. However, the copper valence cannot be easily increased very high, since the state of  $\text{Cu}^{3+}$  is relatively unstable thermodynamically. This instability is manifested in these materials as follows: as the Sr concentration increases, the copper valence increases, until a certain maximum value, beyond which further increases in Sr content are accompanied by the formation of oxygen vacancies, which compensate the charges so that the copper valence does not continue to increase. These effects depend strongly on the partial pressure of oxygen during synthesis. For "normal" preparation conditions (either in air or 1 bar of oxygen), the maximum copper valence is approximately +2.15, so that samples can be prepared without oxygen vacancies under these conditions up to  $x \sim 0.15$ . In order to prepare such samples with higher values of  $x$  and no oxygen vacancies, higher oxygen pressures are required. Using pressures of  $\sim 200$  bar, the IBM group extended<sup>2</sup> the range of compounds without oxygen vacancies up to  $x = 0.35$  and  $\text{Cu}^{+2.35}$ . For samples with higher values of  $x$  and correspondingly higher valences of copper, still higher oxygen pressures are required.

The original extension of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$  compounds up to new record values of copper valence of +2.35 was extremely significant for the field of High  $T_C$  Superconductivity: in the previously known samples, as the Sr concentration was increased,  $T_C$  increased up to almost 40K, and looked as if it could be increased even further (Figure 1). Measurements of the new samples showed, however, that  $T_C$  surprisingly decreased with increasing  $x > 0.15$  and actually disappeared for  $x > 0.26$ . This discovery was met with a certain amount of controversy<sup>3</sup>, but it has now been clearly established experimentally<sup>4</sup> that superconductivity does indeed disappear at high  $x$  and that there are no complications of alleged second phases in this region.

## OBJECTIVES

But what happens at higher values of  $x$ ? i.e.  $x > 0.35$ ? The remaining range of unknown compounds is four times as wide as what has been measured up to now. There is no published ideas or predictions of what type of superconducting behavior could be found in this unexplored region. It is the objective of this work to extend this frontier and explore the unknown region. Synthesis of these compounds is a straight forward, but difficult experiment. Since these compounds are known to exist,

it is perhaps the most promising proposal to make new copper oxide materials. It is made possible by IBM's new experimental capabilities: a new high pressure oxygen pressure furnace, able to synthesize oxide samples at pressures up to 20Kbar and at temperatures up to 1100C.

## RESULTS

### A. Phase Separation

The strategy adopted was to first synthesize the compounds from elemental oxides at relatively low pressure and form the desired  $K_2NiF_4$  structure, albeit with a high concentration of oxygen vacancies. The second step consists of annealing these structures at high partial pressures of oxygen in order to fill those vacancies. From a close examination of the X-ray diffraction patterns of several of the initial samples (see Figure 2), it was discovered that the material system was not a solid solution, but exhibited phase separation in the large x region. In order to understand this behavior, the samples were examined in more detail and the phenomenon was mapped out as shown in Figures 3 & 4.

Clearly, the phase boundaries depend on the partial pressure of oxygen, with high pressures favoring the desired  $K_2NiF_4$  phase of  $La_{2-x}Sr_xCuO_{4-\delta}$ . The second, high x phase appears to be one with  $x \sim 1.3$ , similar to those originally described with superstructure seen in the TEM images<sup>1</sup>. It took considerable time to map out these regions of phase separation, since the time to come to equilibrium was apparently extremely long, even at high temperatures.

### B. Annealing

After the discovery of the complications due to phase separation, the synthesis strategy was modified. Initially, compounds were prepared from oxides at 1050C, using 100 bar of oxygen pressure (in a special high pressure furnace at IBM), a region of Figure 4 where the samples are single phase. Then, these samples were annealed in oxygen partial pressures up to 15 Kbar at various temperatures, for varying length of time. The copper valence was then measured using a special double titration technique<sup>6</sup>, from which the oxygen vacancy content can also be calculated. The results for  $x=1$ , for example, are summarized in Figure 5. Annealing the samples at high oxygen pressure increased the copper valence above its initial value of +2.45, but clearly there is an upper limit of about +2.65 to the valence achievable with this pressure. It was concluded that annealing for about 4 hours at 650C gave optimum results, although there is a relatively wide range of conditions that give similar results.

### C. Copper Valence vs x

The results of the titration experiments are summarized in Figure 6. They could not be completed due to lack of continued support within IBM and from the AFOSR. Nevertheless, the trends are clear: samples prepared under 15 Kbar of oxygen partial

pressure tend to have a maximum copper valence of +2.65 . This value is a considerable increase above the maximum of +2.35 for 200 bar. Using these high pressures thus extends the range of compounds in the system without oxygen vacancies up to  $x=0.65$ , well beyond the previous maximum of  $x=0.35$  .

#### D. Superconductivity

The new samples in the range of  $0.35 \leq x \leq 0.65$  were measured at low temperatures. Their resistance showed no evidence of superconductivity down to 7K.

### CONCLUSIONS

Using a special high oxygen pressure furnace, a series of new compounds were synthesized in the system  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ . These experiments enabled the synthesis of samples without oxygen vacancies at higher values of Sr concentration than possible before. In fact, the range of such compounds was almost doubled, from  $0 \leq x \leq 0.35$  to  $0 \leq x \leq 0.65$  . However, the new copper oxide compounds were not superconducting above  $\sim 7\text{K}$ .

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## FIGURE CAPTIONS

Figure 1. Behavior of superconducting transition temperature as a function of Sr concentration,  $x$ , showing large region of  $0.35 < x < 0.1.00$  which has remained unexplored.

Figure 2. X-ray powder diffraction patterns for samples prepared at 1000C with  $x=0.8, 0.9$ , and  $1.0$ , showing presence of two phases for latter two compositions.

Figure 3. Temperature ranges where samples can be prepared in air as single phase (solid symbols) and regions of phase separation (open symbols). (Squares from Nguyen et al.; up-triangles from deLeeuw et al.; down-triangles from Takagi et al.; diamonds from Torrance et al.; and circles from this work.)

Figure 4. Temperature range where samples can be prepared at 100 bar as single phase (solid circles), showing a smaller region of phase separation than for samples prepared in air.

Figure 5. Measured copper valence for annealing experiments at 15 Kbar for various temperatures and times. Hatched area gave maximum copper valence.

Figure 6. Measured copper valence vs Sr concentration ( $x$ ) for samples synthesized under different oxygen partial pressures. Preparing samples under 15 Kbar clearly extends the range of compounds without oxygen vacancy up to  $x=0.6$ , nearly twice the available range previously prepared at 200 bar.

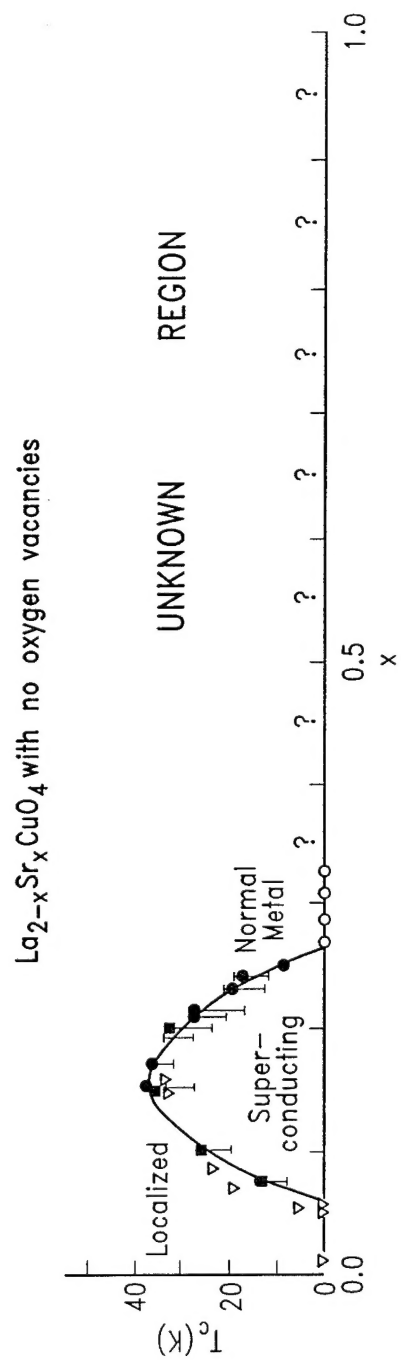


Figure 1

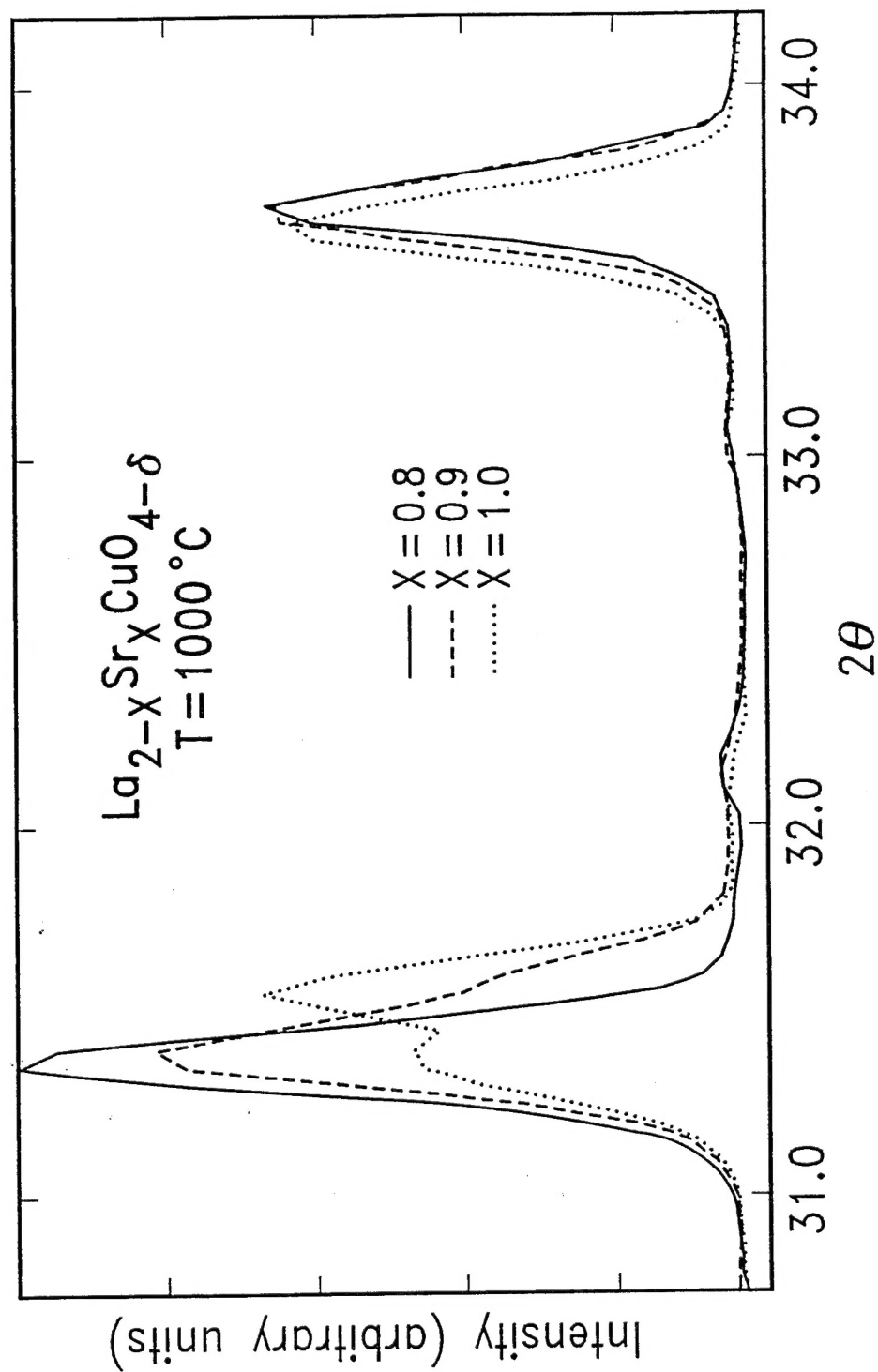


Figure 2

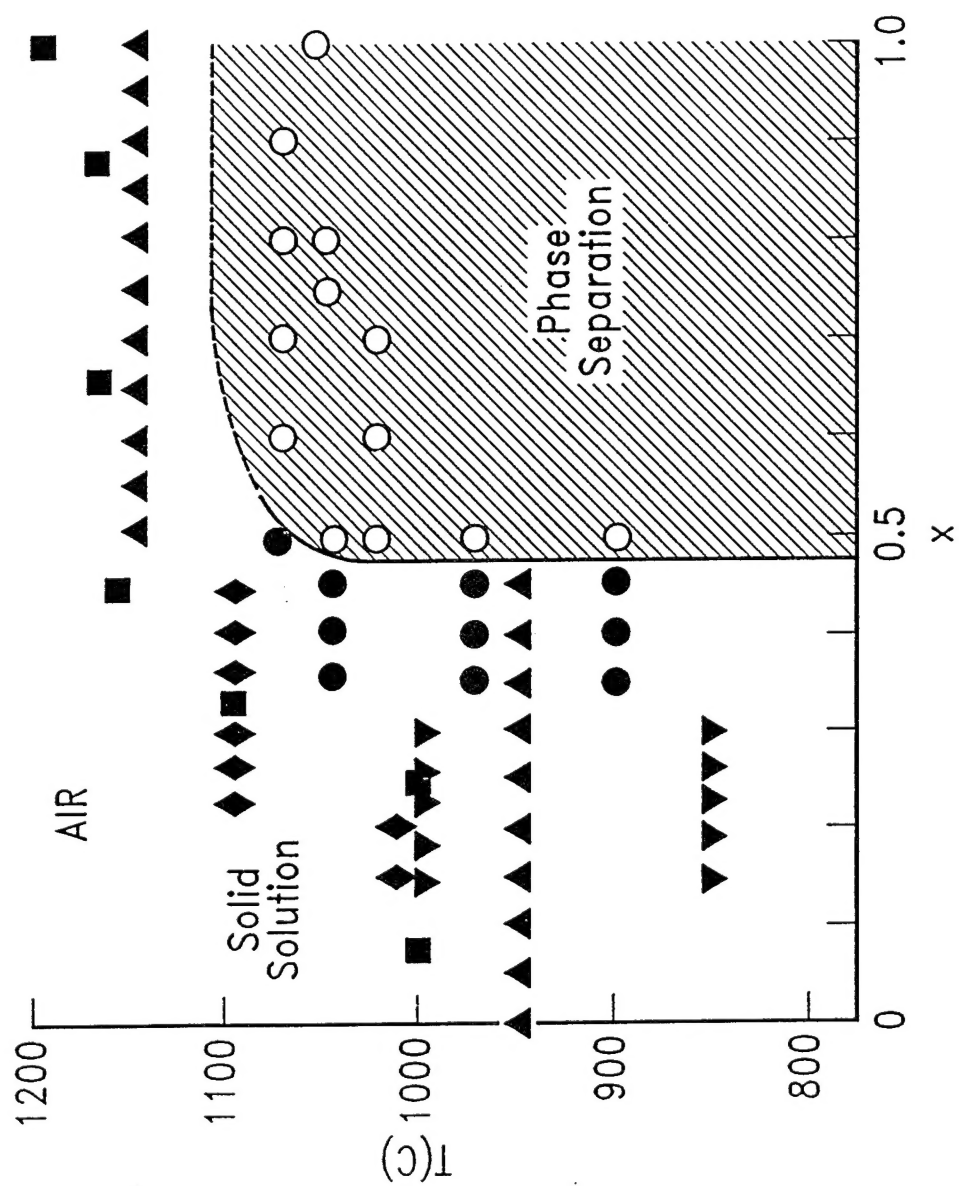


Figure 3

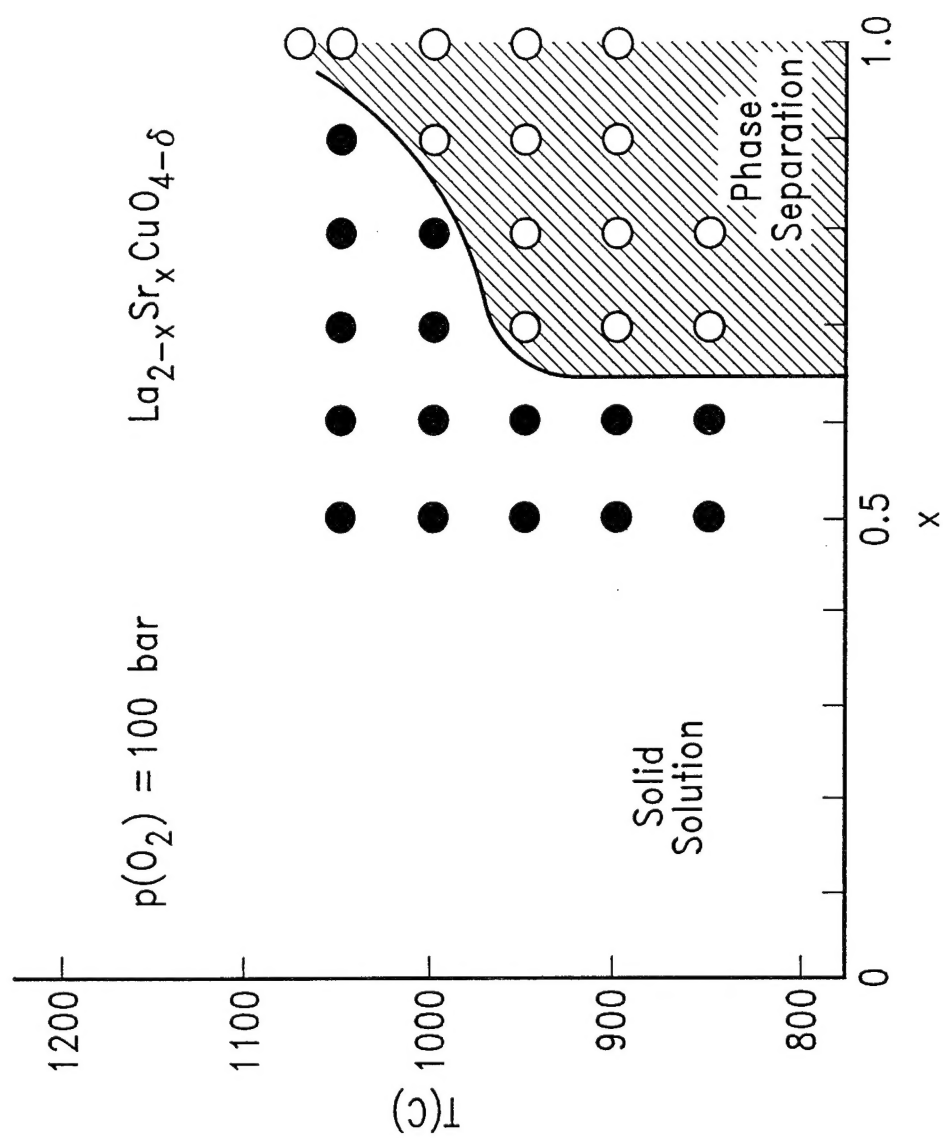


Figure 4

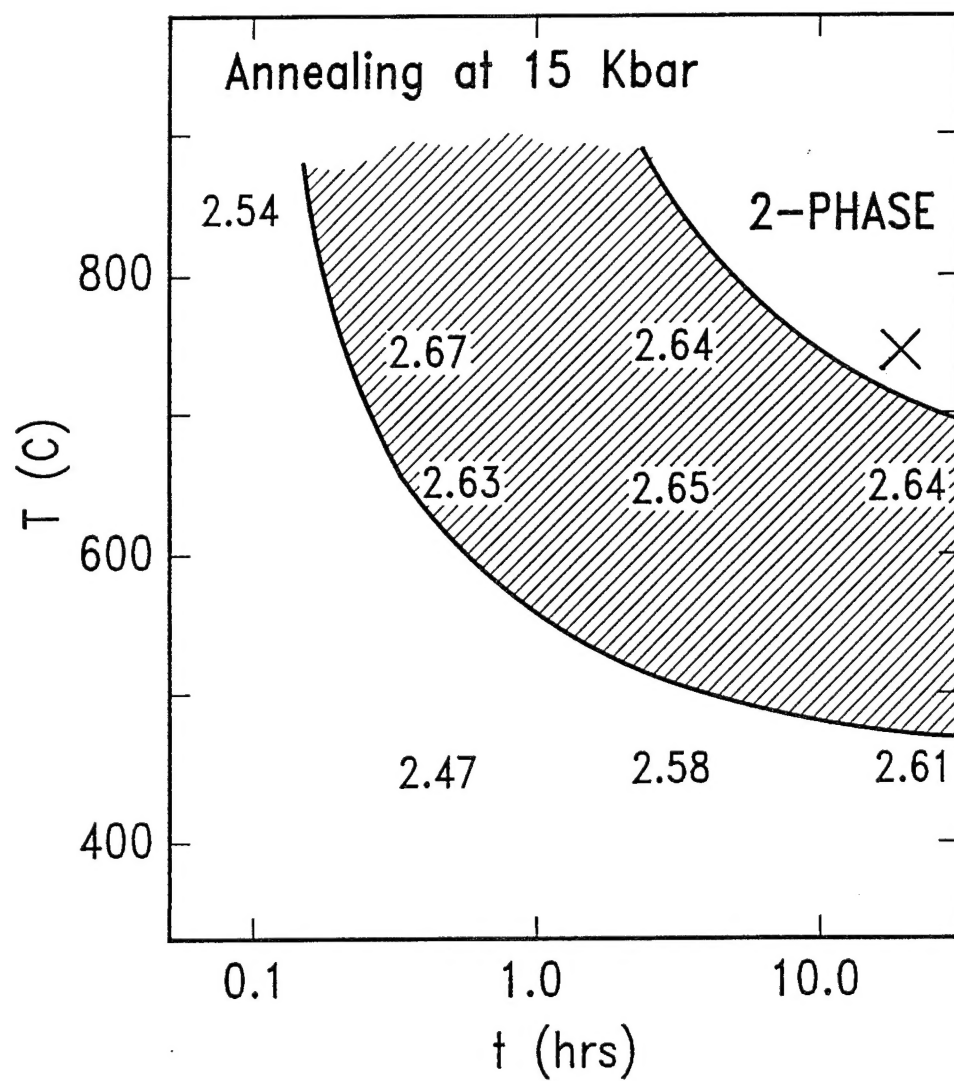


Figure 5

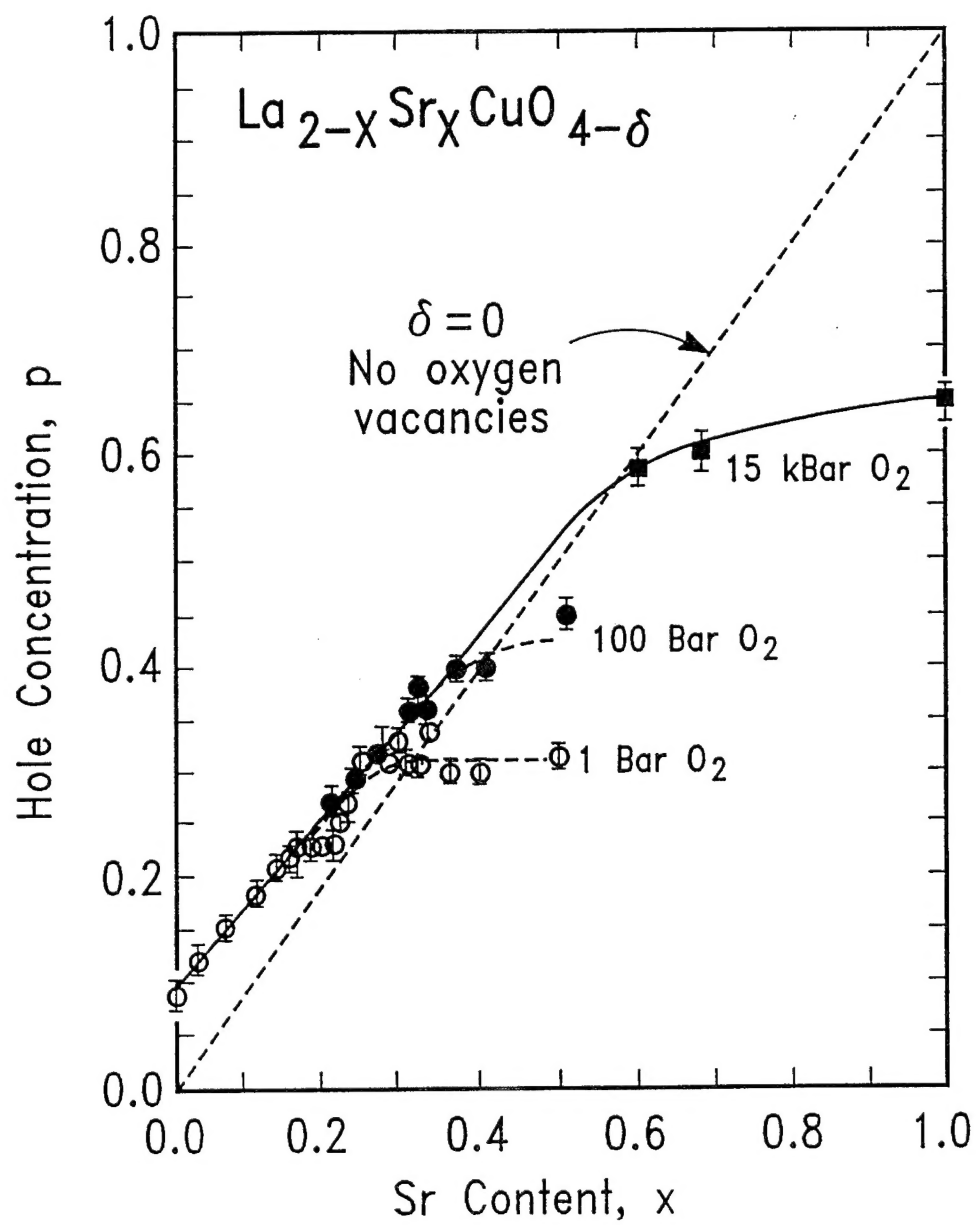


Figure 6